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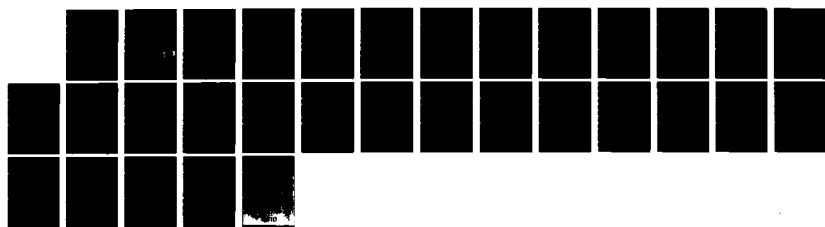
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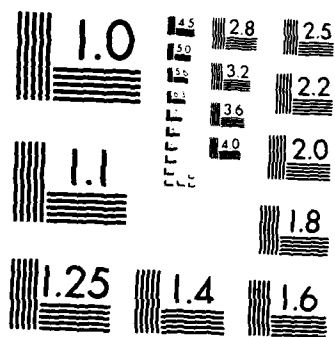
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NONDESTRUCTIVE FT-IR SAMPLING TECHNIQUE
TO STUDY GLASS FIBER COMPOSITE INTERFACES

by

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Abstract

5-11-11
— A nondestructive FT-IR sampling technique was developed to study glass fiber composites. Two coupling agents, γ -APS (γ -aminopropyltriethoxysilane) and γ -MPS (γ -methacryloxypropyltrimethoxysilane) were used to test the validity of the technique. The spectra obtained were compared with those obtained using the KBr pellet and diffuse reflectance techniques. The new technique was sensitive to changes in the coupling agent structure induced by heating, changing the drying environment, and pH. This technique could be used to monitor surface treatments on glass mats or to do quantitative studies of such systems in the 3800 to 1100 cm^{-1} range of the mid-infrared spectrum. ←

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Introduction

Many techniques have been used to study composite materials [1], but none yield as much information about the structure of the coupling agent as does infrared spectroscopy. With the advent of Fourier transform infrared spectroscopy (FT-IR), the usefulness of infrared spectroscopy for the study of surfaces was greatly enhanced. FT-IR spectroscopy is now routinely used to study the molecular structure of coupling agents on various substrates including silica [2-6], metals [7-12], and fillers [13].

There are two main methods of preparing composite samples for transmission infrared analysis. One method is to grind finely the sample in KBr and press the powder into a transparent pellet. Alternatively, one can grind the sample in nujol mull and evenly disperse the mixture on a salt plate. Of the two methods, the KBr pellet technique is the most commonly used. KBr has no absorption bands in the mid-infrared region of the spectrum which interfere with the substrations, but nujol does.

Although the KBr pellet technique is very widely used, it has certain disadvantages [14,15] for the study of composites which must be considered carefully. First, grinding the composite into a powder of small particles and exposing the resulting mixture to tremendous pressures when making the pellet could certainly influence the structure of the coupling agent. Bonds could be broken or new species could be formed when using such a preparation technique. Secondly, KBr (or any alkali salt) is very hydrophilic. The salt will adsorb water or moisture from the atmosphere. Grinding only increases the amount of surface area, in turn increasing the amount of water present in the pellet. But more detrimental is the fact that the salt will remove water that is naturally present in the sample. Finally, one must be very careful to reproduce precisely the grinding procedure because the final

particle size can, and does, affect the intensity and frequency of the infrared band [14]. This consideration is critical when one is planning quantitative studies.

The KBr pellet technique is widely used because the other infrared sampling techniques for composite studies have severe limitations. The internal reflection technique cannot be used for quantitative studies because it is difficult to reproduce the amount and pressure of the contact between the sample and the internal reflection element [16]. Only the interaction between the coupling agent and a metal surface can be studied with the reflection absorption technique [17]. Photoacoustic spectroscopy shows promise, but the quantitative nature of the technique remains suspect [18]. The main drawback of the diffuse reflectance technique is that any IR modes of the substrate which strongly absorb IR radiation mask the surface species information in those overlapping regions of the spectrum. As can be seen, all the techniques have their own particular drawbacks. The purpose of this study was to find a way to conduct an infrared spectroscopic study of the composite in its natural environment.

Experimental

The coupling agents used in this study, γ -aminopropyltriethoxysilane (γ -APS) and γ -methacryloxypropyltrimethoxysilane (γ -MPS), were purchased from Petrarch Systems Inc. The coupling agents were used as received without further purifications.

The E-glass mats used in this study were supplied by the Crane Glass & Company, and had two different thicknesses; one was one-half as thick as the other. The E-glass mats have a surface area of 0.5 sq.m./g. The glass mats were heat cleaned at 500°C for 24 hours in a high temperature oven to remove binders and other impurities.

The γ -APS coupling agent was hydrolyzed in deionized distilled water for 30 minutes. The concentration range of 0.1% to 5% by weight was studied. A suction filtration apparatus was constructed using a fine grade glass fritted filtration funnel. Two layers of glass mat were placed on the bottom of the funnel. The hydrolyzed coupling agent solution (approximately 40 ml) was added and allowed to interact with the glass mats for three minutes. After three minutes, the excess coupling agent solution was removed by vacuum suction for ten seconds. The glass mats now treated with coupling agent were dried at room temperature for a minimum of 24 hours. All samples were stored in aluminum foil until analyzed. Distilled water adjusted to pH 3.5 with glacial acetic acid was used to hydrolyze the γ -MPS.

For the pH studies, after the γ -APS was added to the distilled water, the coupling agent solution was adjusted to the desired pH by adding HCl or NaOH solutions. The total hydrolysis time was 30 minutes. A Beckman model 3500 digital pH meter with a standard glass electrode was used to determine the pH values.

Samples not dried in air were dried in a glove bag. Nitrogen gas was used for a CO₂-free environment, and dry ice for a CO₂ saturated environment. Samples were dried in each environment for 24 hours.

The FTS-20E Digilab FT-IR spectrometer purged with nitrogen gas was employed to collect the infrared spectra. All spectra were recorded in the absorbance mode with double precision at a resolution of 2 cm⁻¹. Usually 200 scans of both the sample and reference were collected to achieve a better signal-to-noise ratio. The frequency was calibrated to an accuracy of better than 0.01 cm⁻¹ with an internal helium-neon laser. All spectra were stored on magnetic tape for future data manipulation. All subtractions were made

using a linear least squares program which yields a scaling coefficient. This coefficient was used to perform the actual subtractions.

Spectra were obtained in the following manner when the No Sample Preparation (NSP) technique was utilized. The glass mats were cut into 1/2 X 1/2 inch pieces and placed in a magnetic sample holder. The reference beam was attenuated and spectra were collected using the double beam option.

When the spectra were obtained by the KBr technique, the samples were ground into a fine powder with infrared grade KBr purchased from Mallinckrodt Company. The mixture was pressed into a pellet for infrared analysis.

A Digilab diffuse reflectance cell (Digilab DRA-100) with two hemispherical mirrors collected the diffuse reflectance spectra. The glass samples studied by diffuse reflectance were not ground in KBr powder. The glass mats were cut to the same size as the sample holders. KBr powder was used as the reference material so that the Kubelka-Munk reflectance plot could be produced. The sample was ratioed against the KBr reference spectrum. All spectra were recorded in the single beam mode. Two hundred scans of the sample were taken.

Results and Discussion

Any technique used for infrared analysis must have a demonstrated validity. The technique must: 1) yield quality spectra; 2) exhibit Beer's law behavior; and, 3) be sensitive to changes in samples (concentration, different coupling agents, etc.). Also, the results obtained must follow known trends in the area of study.

Figure 1 shows the spectra that are obtained when the No Sample Preparation (NSP) technique is used. The difference spectrum of 5% γ -APS on E-glass mats is shown in figure 1C. For purposes of comparison, figure 2 shows the spectrum of γ -APS on E-glass mats obtained by the KBr pellet technique and figure 3

shows the spectrum of γ -APS obtained by diffuse reflectance spectroscopy. Figure 3 also shows the spectra of γ -APS obtained by all three techniques for comparison purposes. The quality of the NSP spectra compares favorably with that of the other two techniques used.

The validity of the NSP technique was easily tested by changing the thickness of the glass mats. The composition of the two mats were identical, except one mat was only one-half as thick as the other. The results of treating with a 2% solution of γ -APS on the two different mats are shown in figure 4. The contribution from the glass has been subtracted in each case. The spectra appear identical. All the bands between 1700 cm^{-1} and 1200 cm^{-1} are clearly visible. Note the absorbance values (A) in this figure which indicate the difference between the maximum and minimum absorbance in the spectrum. In spectrum A, showing the γ -APS coupling agent on the thinner mat, the absorbance value is 4. In spectrum B, however, the spectrum of γ -APS on the thicker mat, the absorbance value is 8. The absorbance value of γ -APS on the thinner mat is exactly one-half that of the A value on the thicker mat. This result is expected since there is twice as much glass present in the thicker mat. The absorbance of the coupling agent therefore depends on the amount of glass present and the concentration of the coupling agent solution [19,20].

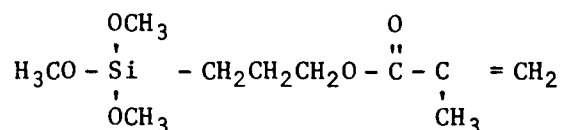
For a transmission study, the most important requirement is that the results are quantitative in nature. In order to obtain quantitative results, Beer's law should be obeyed. Beer's law states that for the same path length a plot of absorbance versus concentration should give a straight line passing through the origin with a slope equal to ϵb .

$$A = \epsilon bc$$

Figure 5 shows the results of the calibration of γ -APS on E-glass mats of different thicknesses. The concentration range was from 1 to 5% by weight which

exceeds the concentrations normally used in industry [1]. The areas of the bands were plotted against the concentration of the coupling agent solution used to prepare the sample. The results show there is a linear relationship between the concentration and the area of the peaks, but the line does not pass through zero as required by Beer's law. When concentrations below 1% were used, the results shown in figure 6 were obtained. A break point occurred at approximately 0.7% concentration. Although not enough data points were obtained to locate accurately the position of this break point, these results indicate that a break point must be present. This behavior has been demonstrated by Ishida et al. for γ -APS [4], γ -MPS [21], and vinylsilane [20] coupling agents. The current explanation for the break point is that at low concentrations the molecules are isolated, but at higher concentrations the molecules begin to polymerize partially. The rate of adsorption of these two species are different, causing a break point in the calibration curve.

A further test of the validity of the NSP technique was provided by using a coupling agent other than γ -APS. γ -MPS (γ -methacryloxypropyltrimethoxysilane):

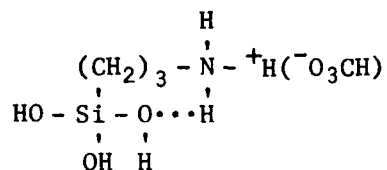


another popular coupling agent used with polyester resins [22], was chosen for this purpose. Figure 7 shows the results of this experiment. In figure 7, one sees a comparison of the difference spectra of γ -MPS (top) and γ -APS (bottom) on E-glass mats. As anticipated the spectra γ -APS and γ -MPS are very different. The top spectrum (γ -MPS) is characterized by the carbonyl peak at 1720 to 1700 cm^{-1} , the C=C band at 1635 cm^{-1} , the methacryl group bands at 1350 cm^{-1} , and the propyl CH_2 groups near 1440 cm^{-1} . These peak positions are very characteristic of the γ -MPS coupling agent [23]. This result confirms that the observed

bands are due to the spectrum of γ -MPS. The splitting of the 1700 cm^{-1} carbonyl peaks shows that a large portion of the γ -MPS is hydrogen bonded to residual silanols in the coupling agent interphase.

Finally, the γ -MPS coupling agent was used to treat the two thicknesses of E-glass mat in the concentration range of 0.5 to 1.5% to see whether the γ -MPS would yield linear calibration curves. The results of this study are shown in figure 8 for the 1720 cm^{-1} and the 1630 cm^{-1} band of γ -MPS. Although only a few points were included, it can be seen that the fit is good, although the line does not pass through the origin. The break point for γ -MPS has been reported to occur at 0.4% concentration by Ishida [21].

The usual method of obtaining infrared spectra of coupling agents on E-glass mats and other materials is to grind a small amount of the glass treated sample in KBr and press the resulting mixture into a transparent pellet [2-6]. A difference spectrum of the γ -APS coupling agent on a glass surface obtained in such a manner is shown in figure 2. In the past, the main area of controversy over this coupling agent concerned the band assignments in the 1700 to 1200 cm^{-1} region of the spectrum for γ -APS. Recently Naviroj et al. [2] determined that the complexity of the bands in this region of the spectrum was due to the formation of a bicarbonate salt between the primary amine of γ -APS and carbon dioxide in the air:



The shoulder at 1630 cm^{-1} has been assigned to the HCO_3^- mode of the bicarbonate salt. The strong bands at 1575 and 1480 cm^{-1} are assigned to the antisymmetric and symmetric deformation modes of the NH_3^+ group. The band at 1330 cm^{-1} has been assigned to the bicarbonate salt, although a certain component of the 1330

cm^{-1} band is undoubtedly due to the CH_2 bending mode of the propyl chain of γ -APS. This assignment was supported by the observation that samples prepared in a nitrogen atmosphere did not exhibit these bands [2].

Figure 1 shows that the No Sample Preparation (NSP) technique yields similar results to those obtained by the KBr pellet technique. Spectrum A is of 5% γ -APS on E-glass mats. Spectrum B is of heat cleaned E-glass mat. It should be noted that spectra A and B are recorded in the absorbance mode, but are similar to the transmission spectra from 2000 cm^{-1} to 1200 cm^{-1} . This effect is caused by the differences in refractive index between the E-glass mats and air when infrared radiation is transmitted through the sample. The peaks in this region are inverted. This is unusual for KBr spectra because alkali halide salts are used to correct for the large difference in the refractive indexes between the samples and air [14,15]. Spectrum C shows the result of subtracting spectrum A from spectrum B. When spectrum C of figure 1 is compared with figure 2, one sees that all the major peaks are present in both spectra, but the band shapes of the two spectra are quite different. In the 1700 to 1200 cm^{-1} region of the NSP spectrum the bands are better resolved (separated) compared with the KBr pellet spectrum in figure 2 where two of the bands appear as shoulders. The high frequency region of the NSP subtraction spectra has a lower signal-to-noise ratio than the KBr spectrum. This is due to the effects of light scattering [24] caused by light passing through the E-glass mat. Although the spectrum is somewhat noisy in this region, one can distinguish peaks. In contrast, the KBr pellet technique yields a large peak due to adsorbed water in KBr powder near 3500 cm^{-1} . Also, the bicarbonate and amine (overtone) in the 2000 to 2700 cm^{-1} are barely distinguishable in the KBr pellet spectrum, while it is clear that these bands are present in the same region of the NSP spectrum.

It seems certain that any water interactions with the coupling agent will be masked by the KBr pellet technique. A strong broad peak near 3500 cm^{-1} in figure 2 shows this. It is possible that some of the frequency differences observed between the subtraction spectra in figures 1 and 2 are due to differences in hydrogen bonding interactions with water, and also differences in the refractive index which are known to cause frequency shifts in the spectrum [15].

Recently a surface-specific technique for the mid-IR range of the spectrum has been revived by the use of the Fourier transform infrared technique. The technique is called diffuse reflectance spectroscopy [25-27]. The diffuse reflectance technique is based on scattering of light by the sample which is collected and analyzed by the Kubelka-Munk theory and yields a reflectance spectrum which resembles an absorbance spectrum. We have also utilized this technique. A 5% γ -APS coupling agent solution was prepared and used to treat an E-glass mat. The infrared spectrum of the coupling agent on E-glass mats was obtained by the three different techniques available to study coupling agents on glass mats: 1) KBr pellets, 2) NSP, and 3) diffuse reflectance. The results of this experiment are shown in figure 3. The contribution of the E-glass mat has been subtracted in each case. Spectrum A was obtained by the NSP technique, spectrum B was obtained by the Diffuse Reflectance technique, and spectrum C was obtained by the KBr pellet technique (spectra A and C have been analyzed previously). Spectrum B shows the 1620 cm^{-1} bicarbonate band, and both the 1575 cm^{-1} and the 1480 cm^{-1} NH_3^+ band. The bands below 1450 cm^{-1} are not present in the spectrum obtained by the diffuse reflectance technique, however. No bands are seen between 1450 cm^{-1} and 800 cm^{-1} in the diffuse reflectance spectrum because the B-O of the E-glass mat absorbs very strongly in this region of the spectrum, and effectively masks any information that would normally arise due to scattered light [27]. Therefore, only half of the γ -APS bands between

1700 and 1200 cm^{-1} can be studied by diffuse reflectance when the substrate is an E-glass mat. The result shown in figure 3 indicates that the NSP technique yields spectra which are of equal, if not better, quality to those obtained by the other two techniques.

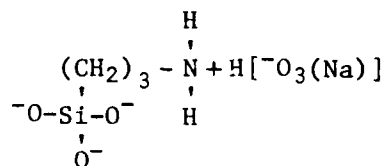
The next experiment performed to test the validity was one where the drying environment of the treated E-glass mats was changed to observe whether the NSP technique is sensitive enough to detect the differences in the spectra reported by Naviroj et al. [2]. Three different drying environments were used. The samples of γ -APS on E-glass were dried in air, nitrogen, and carbon dioxide environments. The difference spectra of γ -APS coupling agent for each of the three environmental drying conditions are shown in figure 9. Spectrum A is of γ -APS dried in CO_2 and spectrum C is of γ -APS dried in air. Spectra A and C are very similar except there is a slight enhancement in the peaks due to the bicarbonate salt: 1630 cm^{-1} , 1475 cm^{-1} , 1330 cm^{-1} , and 1390 cm^{-1} bands. The results of drying γ -APS in nitrogen are shown in spectrum B. There is a marked difference in this spectrum as the contribution of the carbon dioxide has been eliminated. These results are the same as those obtained by Naviroj et al. [2].

The γ -APS coupling agent has an amine functionality, therefore one would expect its structure to be influenced by pH [1]. Another experiment was performed to study the effect of pH on the structures of γ -APS. The infrared subtraction spectra obtained by the NSP technique are shown in figure 10. Spectrum A was prepared at pH 12, spectrum B was obtained at natural pH of 10.8, and spectrum C was obtained at a low pH of 2.

At low pH, the carbon dioxide would be in the form of carbonic acid [28] and it would not be expected to interact with the amine group due to the competition with HCl. Therefore, no effect due to the bicarbonate salt would be

expected in the resulting spectrum. Figure 10C shows the results of low pH. The 1639 cm^{-1} band has disappeared, the 1475 cm^{-1} band has diminished and broadened, (which is characteristic of NH_3^+Cl^- salt which would be formed at low pH), and the 1450 cm^{-1} and 1420 cm^{-1} bands have also disappeared. The intensity of the 1330 cm^{-1} band has diminished and shifted up to 1385 cm^{-1} , again indicating that the bicarbonate salt is no longer present in the sample of γ -APS prepared at low pH.

At high pH of 12, spectrum A, the 1630 cm^{-1} band is no longer observed. The NH_2 deformation peak increases in intensity and shifts to a higher frequency. The NH_3^+ peak is still observed as are all the other bands between 1500 and 1200 cm^{-1} which are seen in the infrared spectrum of γ -APS dried in air and shown in figure 10B. One would expect the amine group to be in the NH_2 form at high pH; this result indicates that more NH_2 is present at pH 12 than at natural pH, but that some carbon dioxide is still present in the sample as evidenced by the peaks from 1500 cm^{-1} to 1200 cm^{-1} . This phenomenon may possibly occur due to a carbonate forming with the amine group at high pH in the form:



This structure would explain the absence of the 1630 cm^{-1} band which is due to the HCO_3^- group but at the same time explains the presence of the other $\text{CO}_3^{=}$ peaks.

Clearly the NSP technique is sensitive to changes in pH and the trends observed follow those that are expected.

If a bicarbonate salt forms with the amine group of γ -APS, then it should be easily removed by heating. This experiment was performed, and the results

are shown in figure 11. The bottom spectrum is of unheated γ -APS. The E-glass has been subtracted out and is shown for comparison purposes. No change with heating is observed until 80°C. Above 80°C substantial changes occur in the spectra of the coupling agent. All the peaks associated with the bicarbonate salt group are greatly diminished after two minutes exposure to heating at 80°C and above. The NH_2 deformation peak at 1560 cm^{-1} is greatly broadened as is the 1320 cm^{-1} peak. This is characteristic of a polymer and it indicates that the coupling agent is cross-linking and becoming cured forming a polyamino-propylsilsesquioxane.

A critical evaluation of the NSP technique reveals that it has the following advantages: 1) it requires no sample preparation, 2) the sample is studied under conditions which are very similar to those of actual use, 3) very low concentrations can be seen (0.1%) fairly easily, and 4) the sample is not destroyed. This technique overcomes the basic problems inherent in the KBr pellet technique; specifically, the sample does not have to be ground up and subjected to high pressures. Since the sample is not destroyed, it is possible to use another technique to study the same sample and compare the results.

The disadvantages of the NSP technique are: 1) the combination of light scattering and refractive index problem, and 2) not the entire mid-IR range can be studied. The refractive index problem shows up in the original spectra, but the difference spectra show only slight wavelength shifts. The light scattering problem results in minor amounts of excess noise in the spectrum. The biggest disadvantage for E-glass mats is that only the region from 3800 to 1000 cm^{-1} can be studied. The strong absorption of the glass below 1000 cm^{-1} interferes with the subtraction process. This means that the information about the Si-O-Si groups is not available with the NSP technique. If thinner glass were used, it is believed that the subtraction problems would be greatly reduced and the region below 1000 cm^{-1} could be studied.

Conclusions

In this study, a new sampling technique was used to examine the interactions between coupling agents and glass mats in a nondestructive manner. The technique is called No Sample Preparation (NSP) because it literally requires no sample preparation to perform the infrared measurements. It has been shown that the technique: 1) can be calibrated, 2) yields results characteristic of the coupling agent when different coupling agents are used, 3) is sensitive to changes in the coupling agent structure (pH, drying conditions, or heating), and 4) yields results which are comparable with those obtained by accepted techniques such as KBr pellets and diffuse reflectance. This technique overcomes the disadvantages of the KBr pellet technique since the sample can be studied in its natural environment and is much easier to use from an experimental point of view. The NSP technique allows one to study the region between 3800 and 1100 cm^{-1} , while the region between 1400 and 1000 cm^{-1} is masked by the glass absorption in the diffuse reflectance technique. This technique can be used easily to monitor the amount and structure of coupling agent on glass mats.

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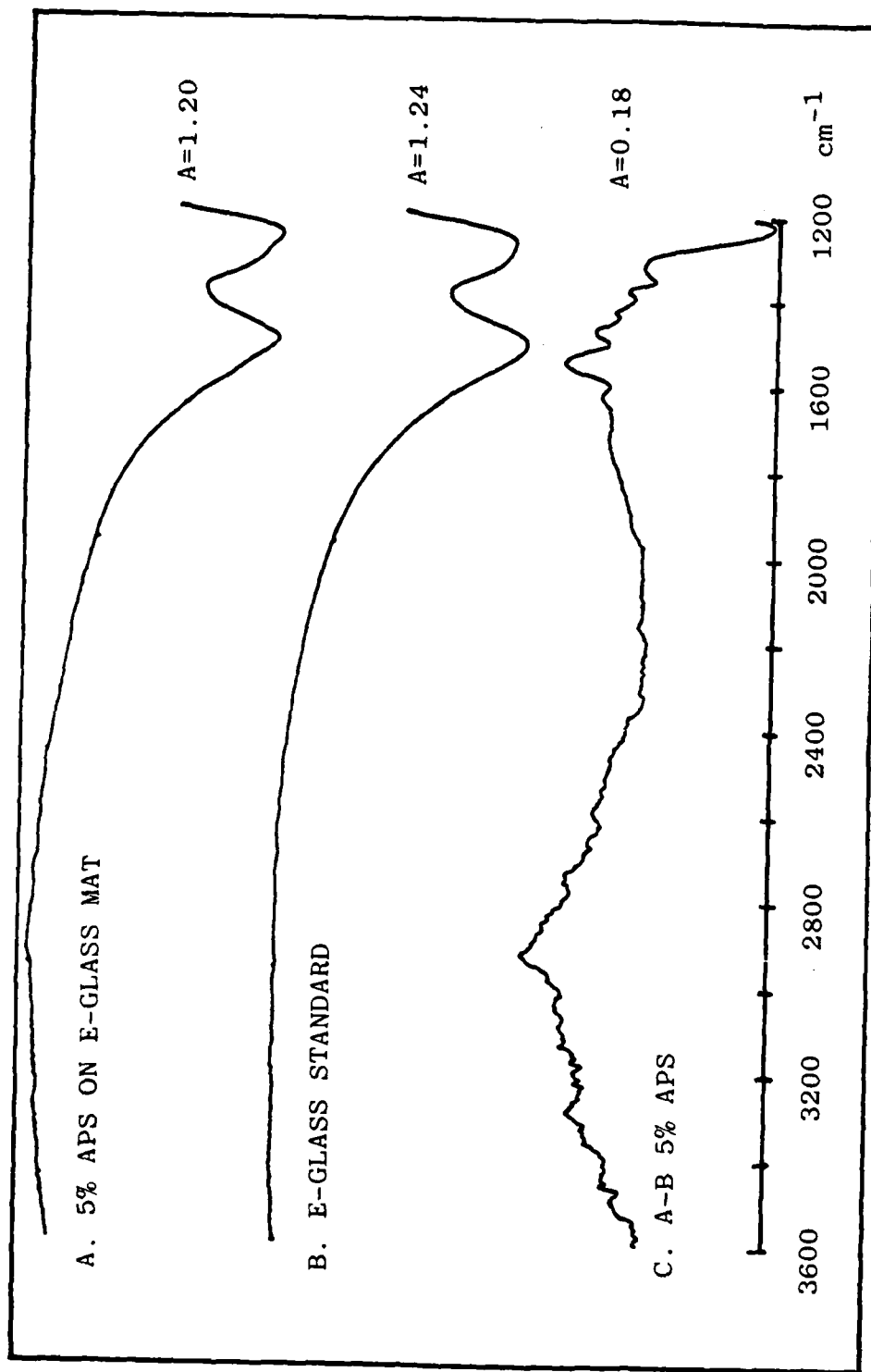


Figure 1. Subtraction process by NSP technique for γ -APS coupling agent on E-glass mats, 5% by weight γ -APS.

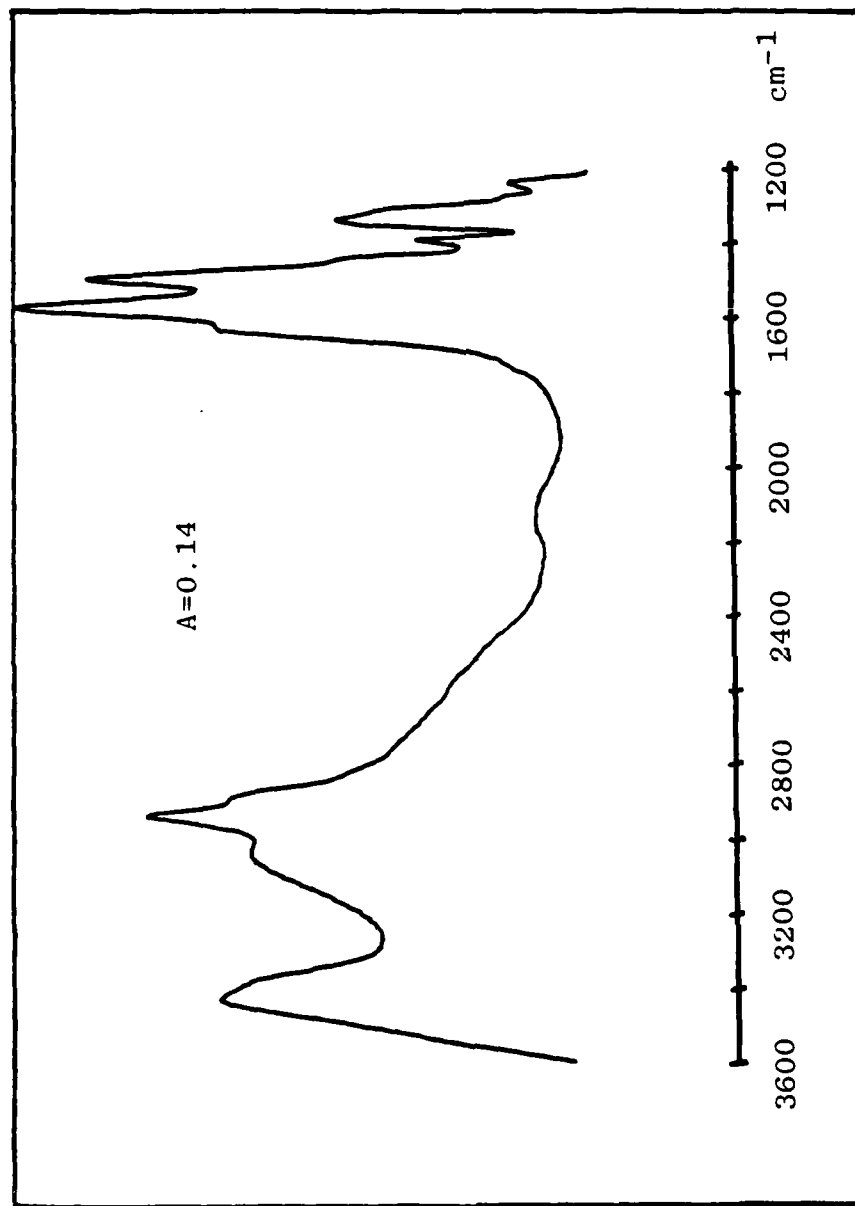


Figure 2. Standard technique of obtaining the spectrum of coupling agent in composite studies, difference spectrum of γ -APS coupling agent obtained by KBr pellet.

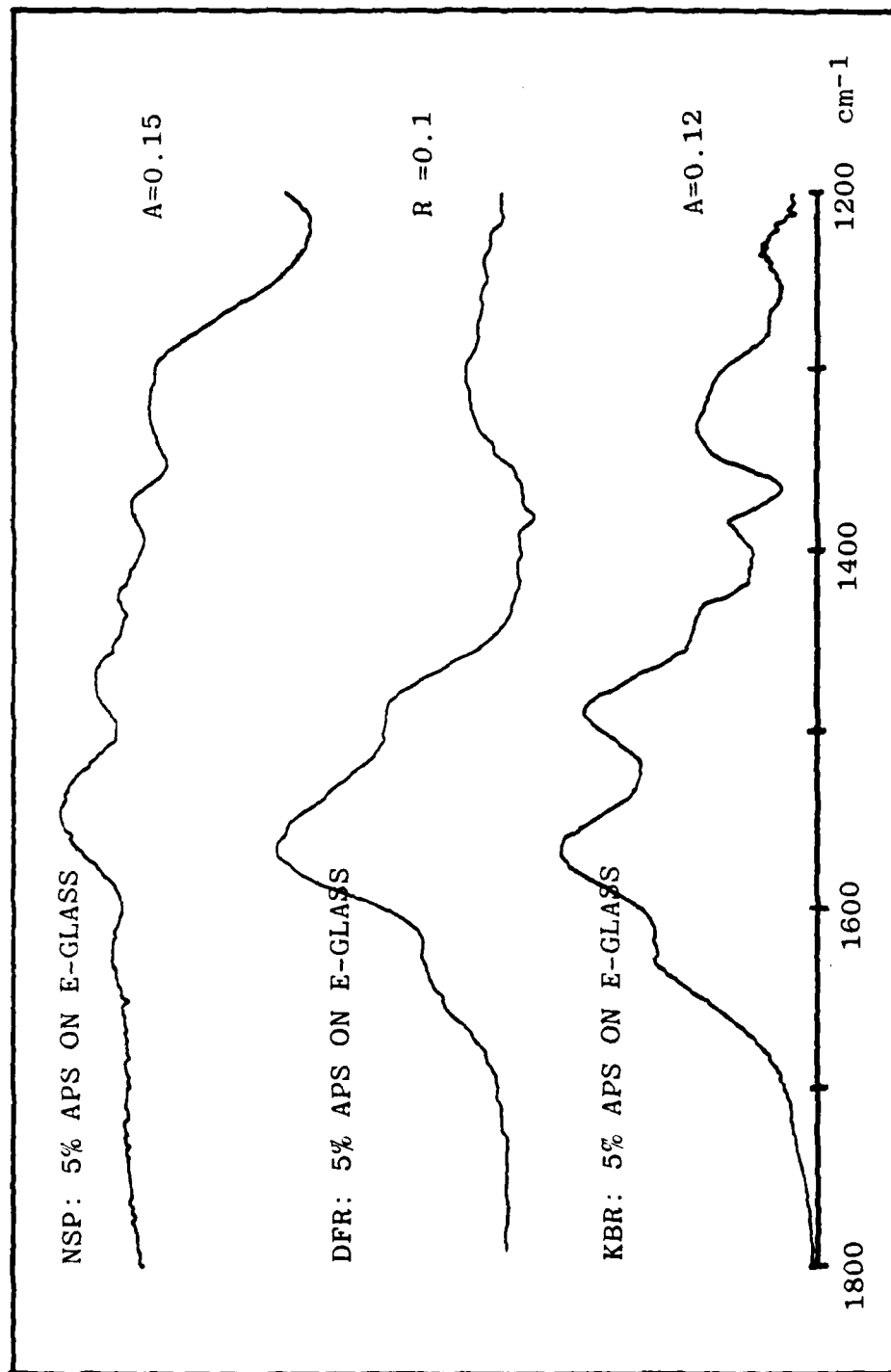


Figure 3. Difference spectra of γ -APS coupling agent on E-glass mats by NSP(top), diffuse reflection(middle), and KBr (bottom).

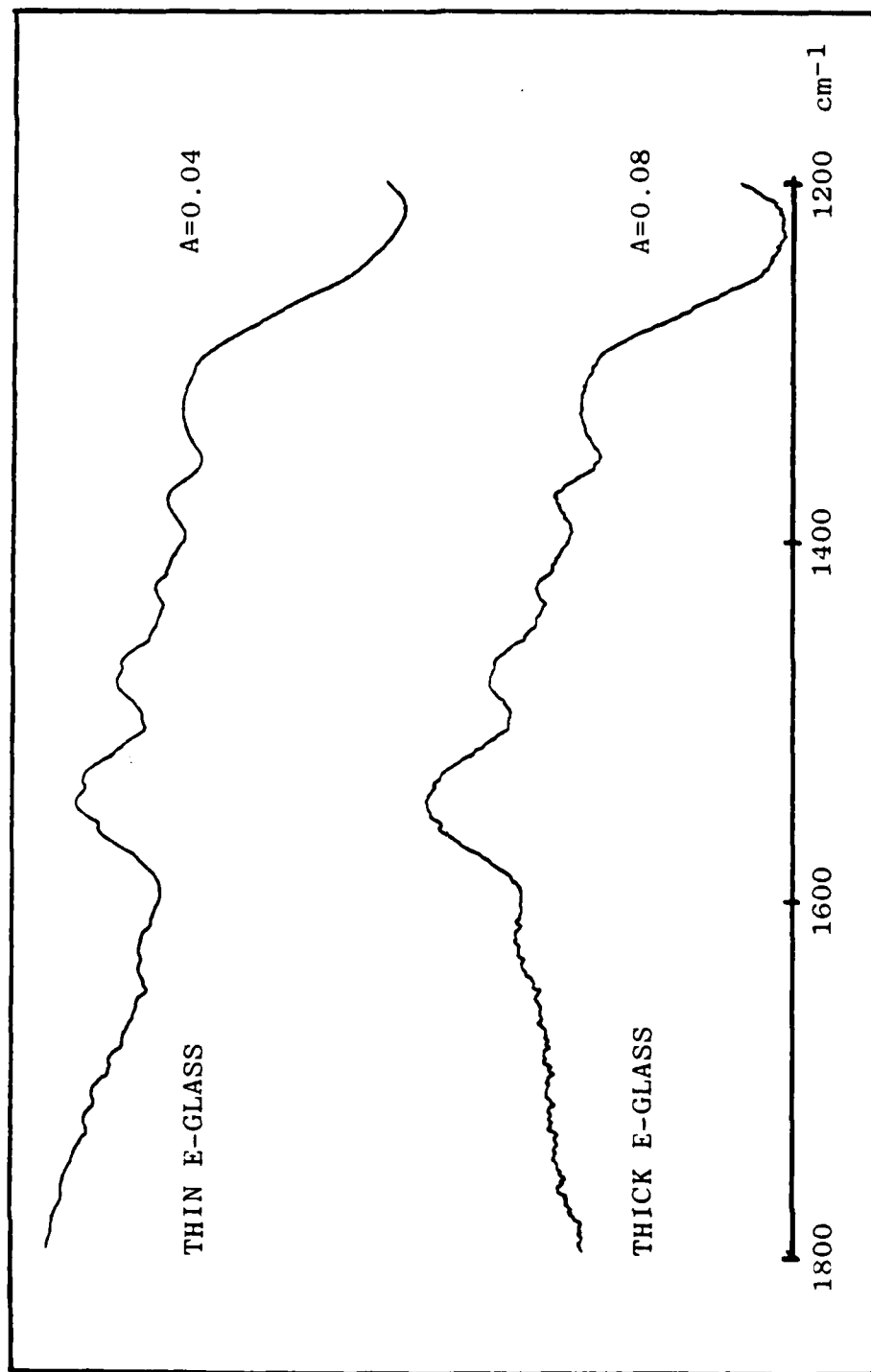


Figure 4. Difference spectra of γ -APS coupling agent by NSP technique on different thicknesses of E-glass mats, 2% by weight γ -APS treating solution.

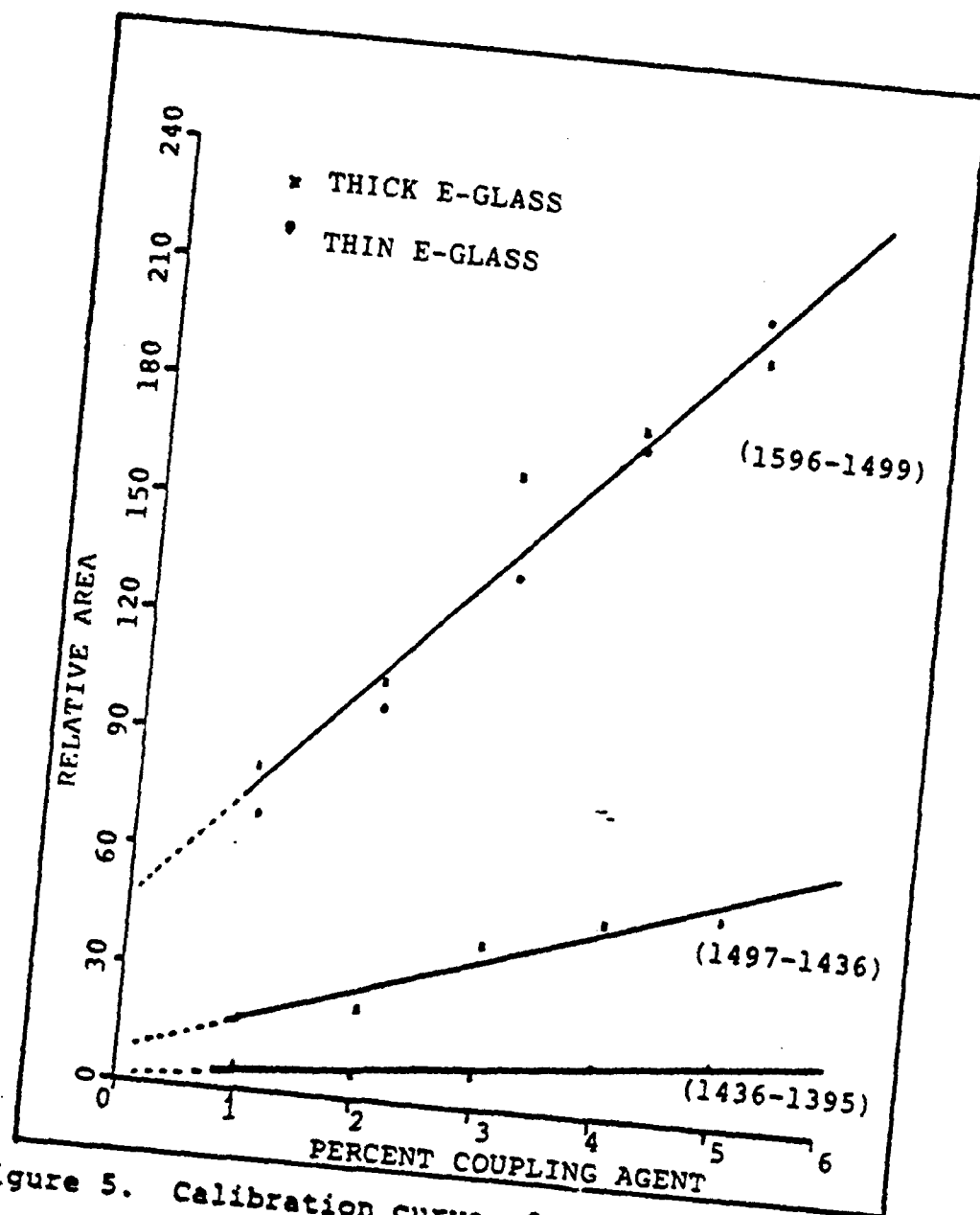


Figure 5. Calibration curve of γ -APS coupling agent on E-glass mats using the NSP technique. Concentration ranged from 1 to 5% by weight.

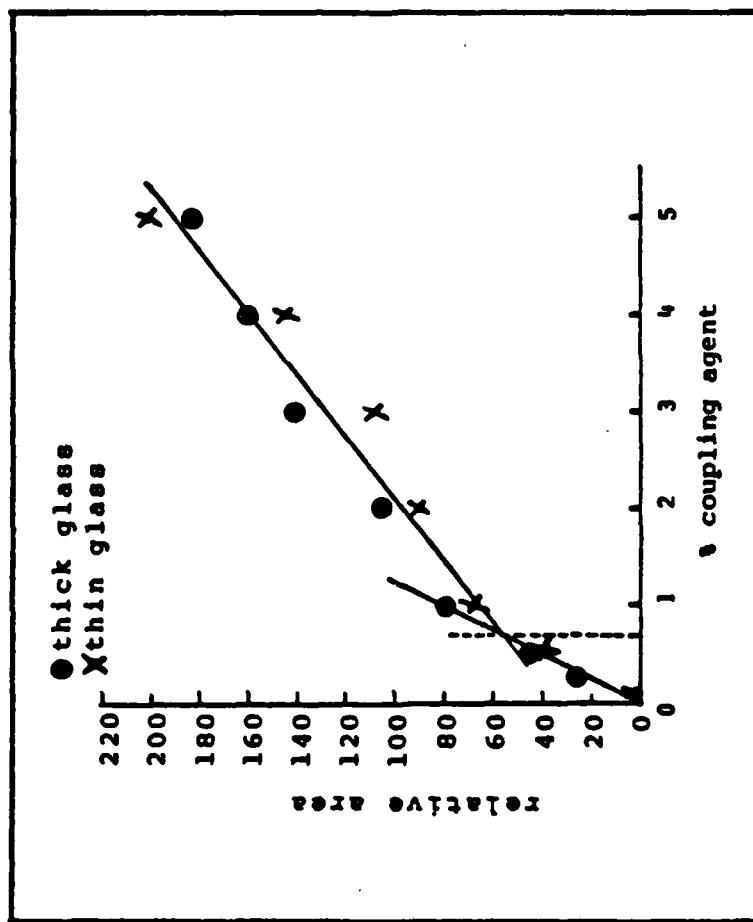


Figure 6. Calibration curve of γ -APS coupling agent on E-glass mats using NSP technique. Concentration ranged from 0.1 to 5%.

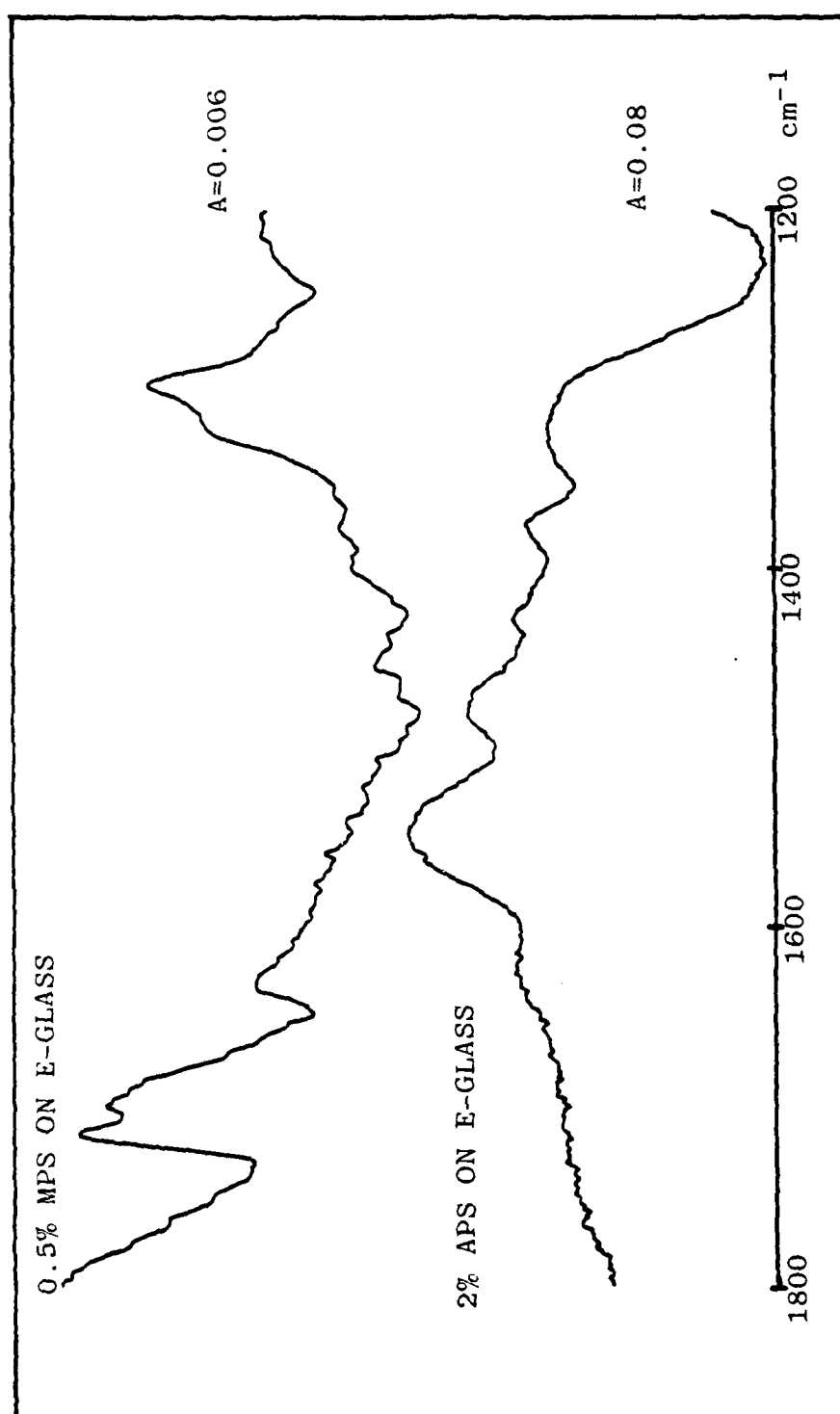


Figure 7. Difference spectra of different coupling agents on E-glass mats obtained by NSP, γ -MPS(top) and γ -APS(bottom).

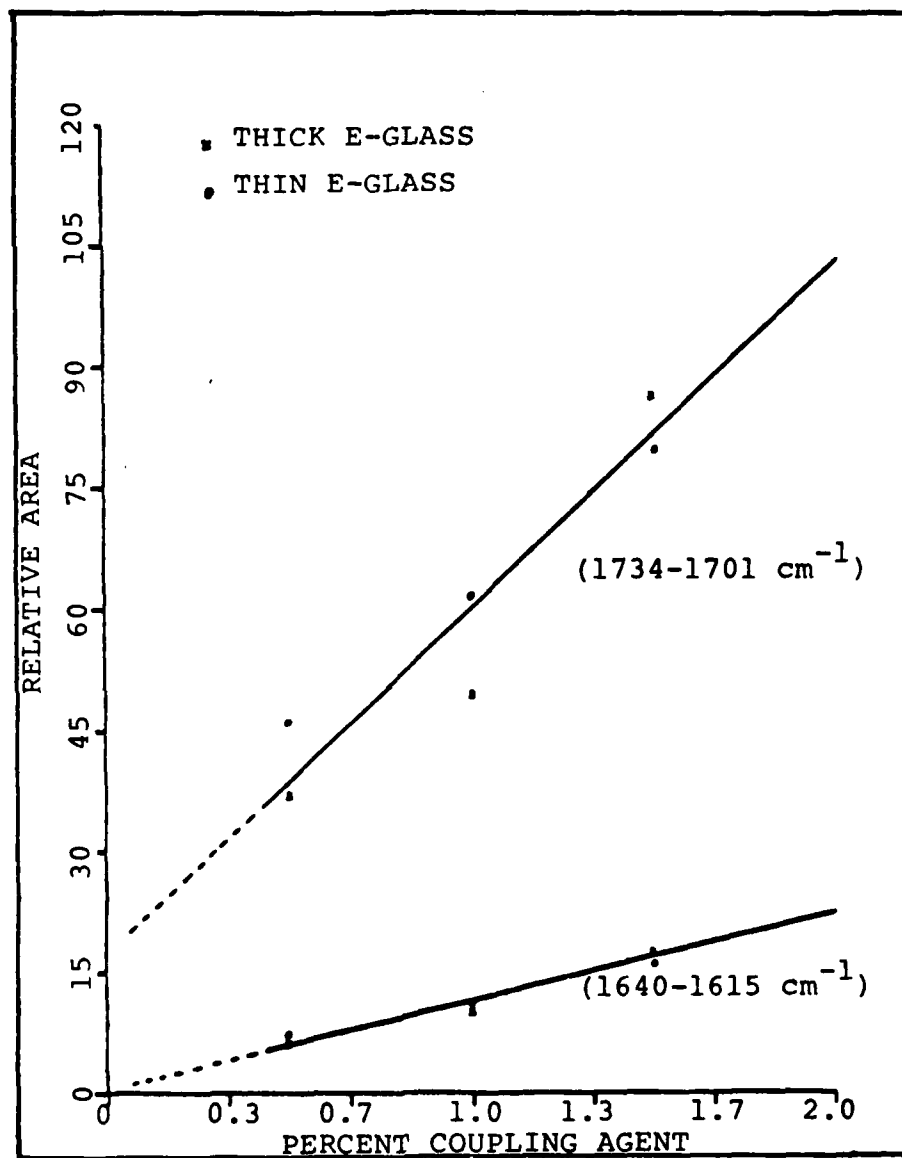


Figure 8. Calibration curve of γ -MPS coupling agent by NSP technique on E-glass mats. Concentration ranged from 0.5 to 1.5% by weight.

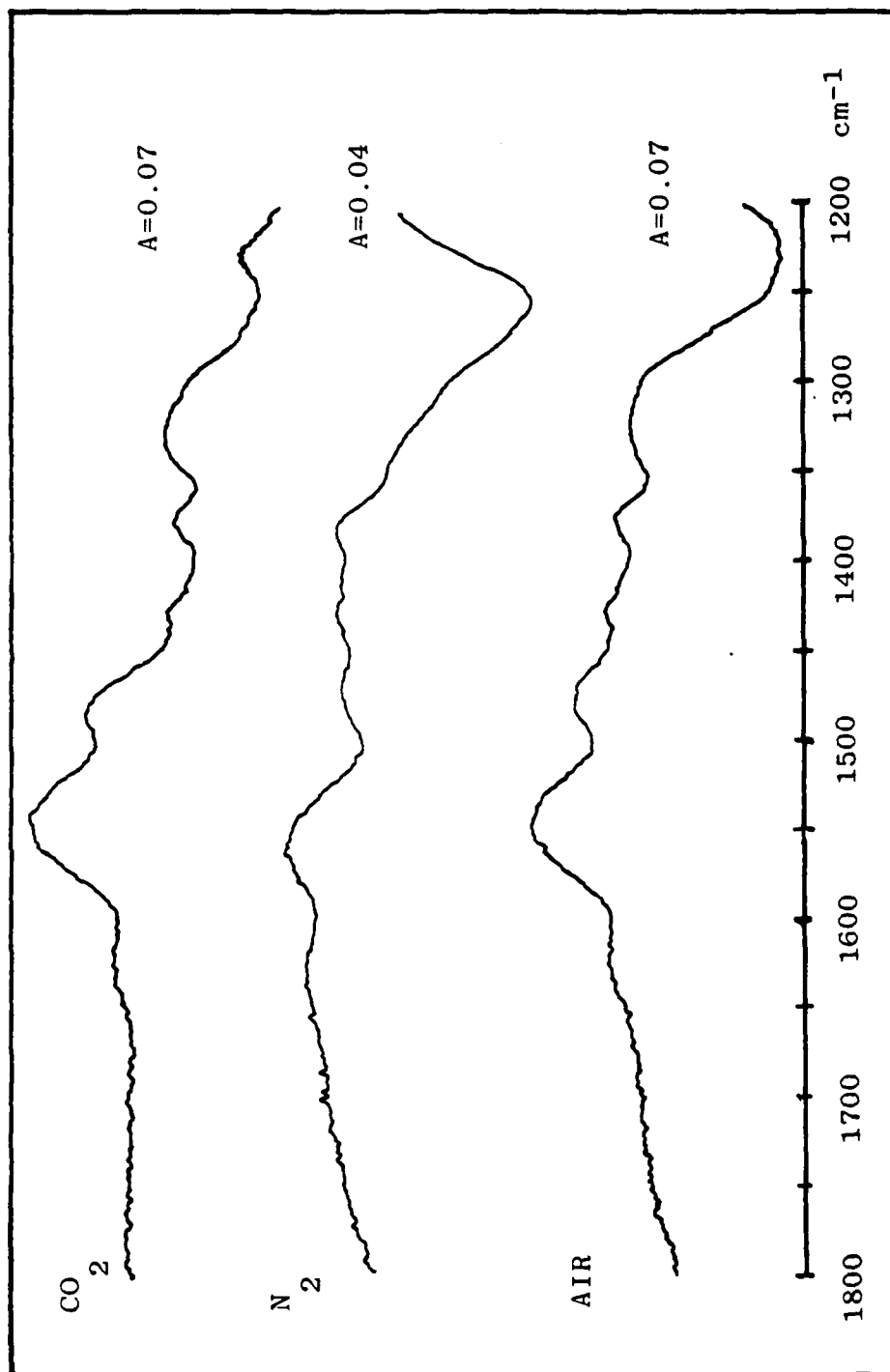


Figure 9. Difference spectra of γ -APS on E-glass mats varying the drying environment collected by NSP technique; CO_2 (top), N_2 (middle), and air (bottom).

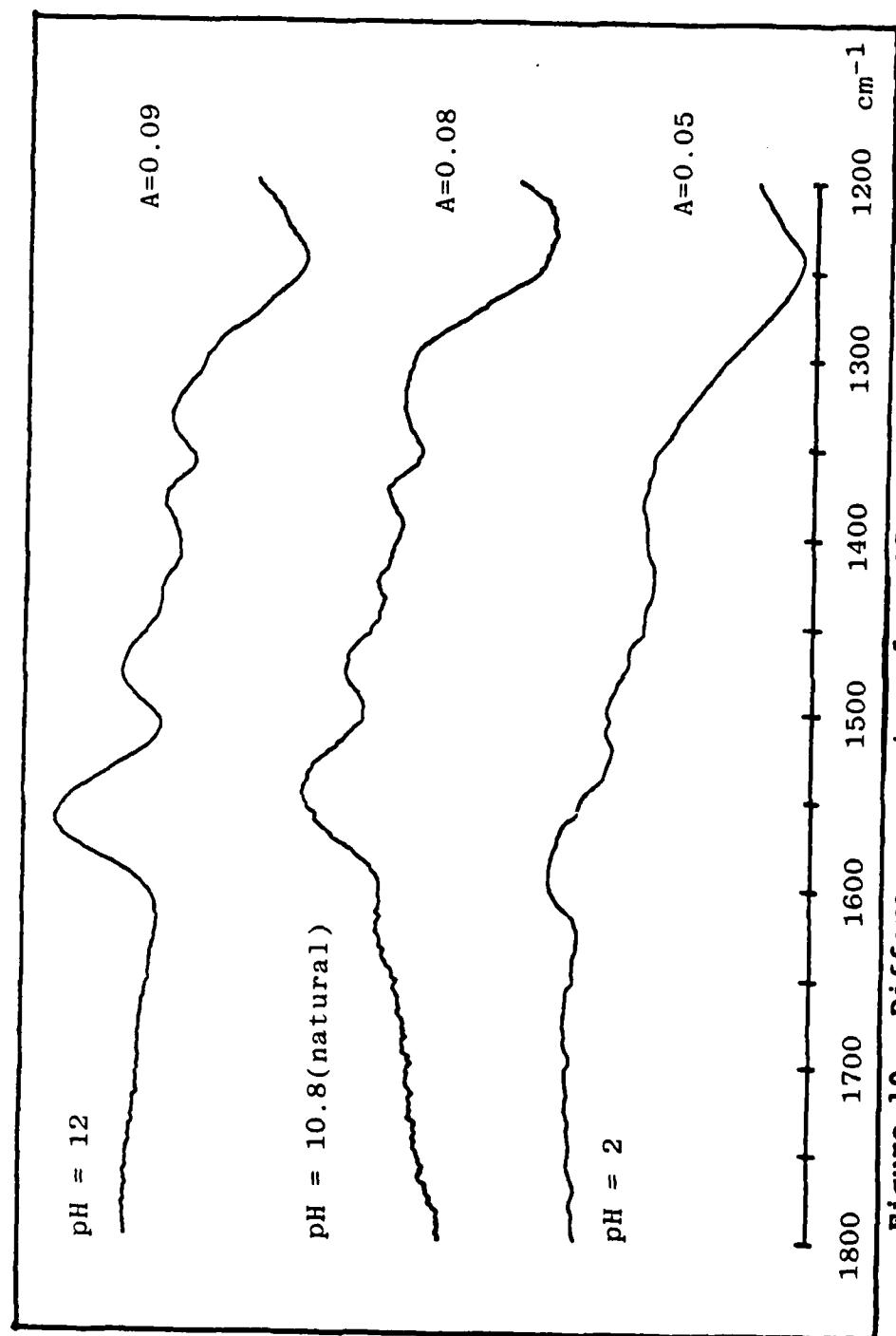


Figure 10. Difference spectra of γ -APS on E-glass mats varying the pH of the coupling agent solution collected by NSP technique; high pH(top), natural pH(middle), and low pH(bottom).

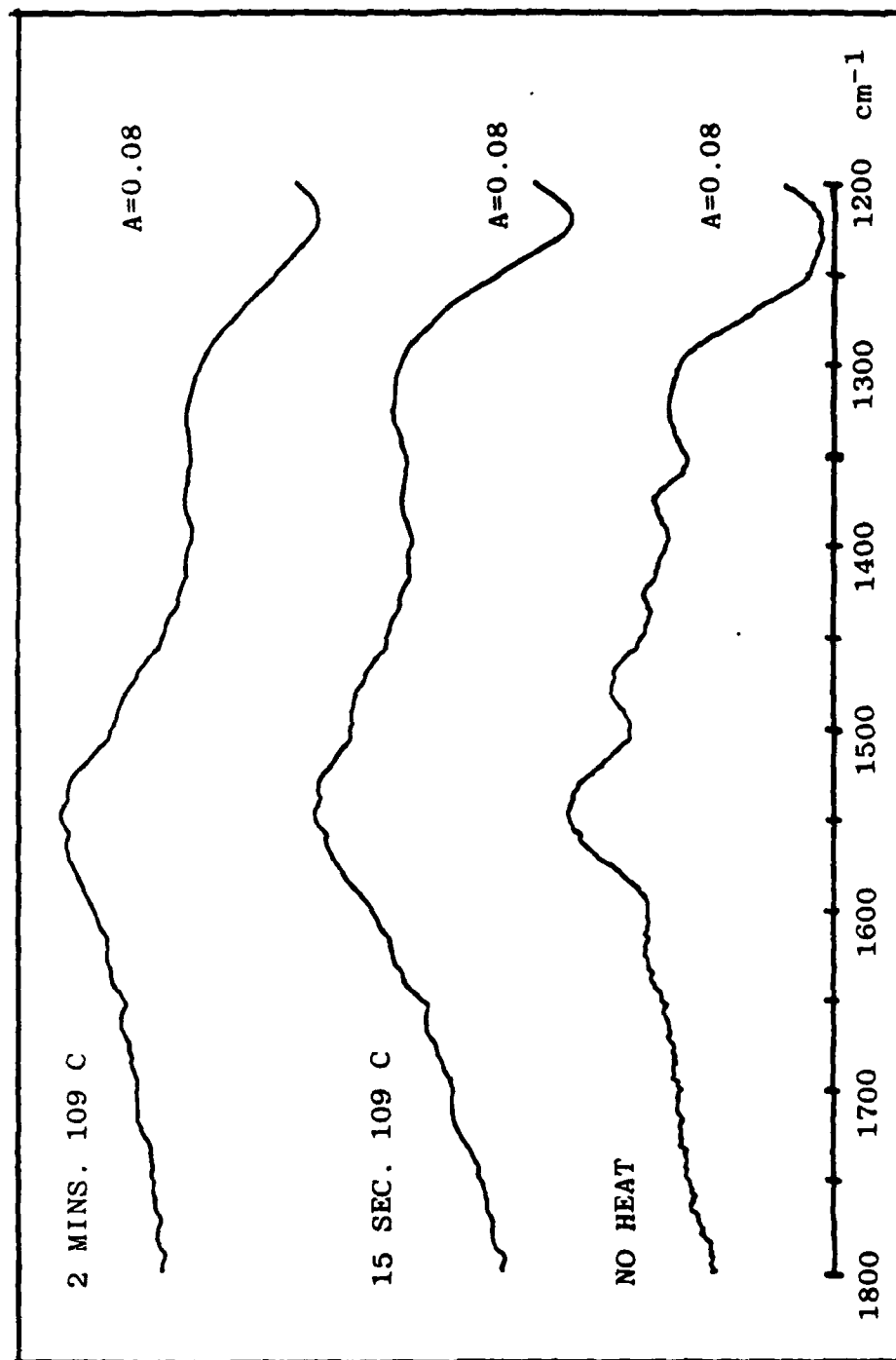


Figure 11. Difference spectra of γ -APS on E-glass mats collected by the NSP technique, showing the effects of heat treatment.

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